

SEGREGATION OF SALT IONS AT AMORPHOUS SOLID AND LIQUID SURFACES

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1 INTRODUCTION

Traditionally, the surfaces of aqueous electrolytes are described as inactive and practically devoid of ions [1, 2]. Indeed, this has turned out to be true for non - polarizable ions, as alkali cations and small anions, as fluoride as well. However, due to polarization interactions singly charged anions, with the heavy halides as particular examples, exhibit a propensity for the water / air (vacuum) interface. This was first suggested in order to rationalize the occurrence of chemical reactions on aqueous interfaces, sea - salt particles, ocean surfaces etc. This initiated MD calculations using polarizable potentials. They suggest that highly polarisable anions can indeed be preferentially adsorbed at the outermost liquid layer. In this description, the ions are polarized by the anisotropy of the interface, creating an induced dipole that is stronger than in the bulk. The interaction between the polarized ions and the surrounding water molecules compensates for the reduced solvation available at the surface. This has triggered a number of laboratory studies, applying mainly non - linear optical probes.

Additional insight into hydration and segregation phenomena would be gained from adsorption experiments on the surface of amorphous solid water (ASW), provided that ASW could be considered as a supercooled extension of liquid water, an issue which is however a matter of active research and intense scientific debate at present [3, 4, 5]. In this case, the entire scope of well - developed vacuum based methods could be applied to the study of the solvation and segregation phenomena at ASW during its annealing above the glass transition temperature T_g . Hopefully, the results would be applicable to surfaces of liquid water as well (where the application of vacuum - based techniques is difficult because of the high vapour pressure of water). Clearly, the study of processes with ASW offers the opportunity to contribute to our understanding of the properties of ASW and its relation to liquid water [6]. First steps into this direction have already been undertaken: The interaction of water, around T_g (136K), -i.e. when the molecular motion in the solvent becomes important, with some polar and nonpolar molecules was studied with TOF - SIMS [7]. It was found that non - polar molecules, hexane as a specific example, are fully

incorporated into the bulk while polar molecules, formic acid for instance, stay at the surface.

Kim et al. [8] examined the migratory motion of Na^+ and Cl^- ions on ASW surfaces by low energy sputtering (LES). The Na^+ and Cl^- populations at the surface were measured as a function of the ASW temperature (100 to 140K). The Na^+ intensity decreased in the range 110 to 130K while the Cl^- intensity remained practically constant. This indicates that the inward migration of Na^+ ions takes place at temperatures where solvent diffusion becomes important, in contrast to surface residence of Cl^- . This surface propensity of certain halides is characteristic for liquid water [9, 10].

The combination of Metastable Impact Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy, UPS(HeI) has been applied to the study of the interaction between halides (CsI, CsF, and NaI) with solid water and methanol around their respective T_g values [11,12]. Surface segregation of iodide, but not of fluoride or Cs ions, took place from ASW, exposed to CsI or CsF vapour, during annealing [11]. The same behaviour was also derived from molecular dynamics (MD) simulations of the corresponding aqueous salt solutions. In contrast, no appreciable surface segregation of ions was observed in methanol under similar conditions, neither in the experiment nor in the simulation of the corresponding liquid solution. It was pointed out that, as far as solvation phenomena are concerned, water and methanol ices, when heated above their respective T_g values, behave remarkably similar to the corresponding liquid solutions. The surface propensity of iodide is also seen when Cs is replaced by Na [12].

In the present report, we present a more through-out analysis of the data for the interaction of halides with solid water and methanol films, in particular those of ref. [12]. This leads to a deepened understanding of the analogy observed between amorphous solids above their T_g and their respective liquid counterparts.

2 EXPERIMENT

The present analysis is based on MIES and UPS (HeI) results presented in [11,12]. The apparatus, applied to the study of the salt - ASW and MeOH interactions, has been described in detail previously [13, 14, 15] (see also [11,12]). It is important for the present analysis that the electrons detected with MIES result exclusively from the outermost layer of the film under study, in contrast to UPS(HeI) which averages over 3 layers, typically. Detailed introductions into MIES and its various applications in molecular and surface spectroscopy) can be found elsewhere [16, 17].

The TPD experiments are carried out using a differentially pumped quadrupole mass spectrometer (QMS), connected to the UHV apparatus employed for the MIES/UPS studies. The ramping time in TPD is considerably shorter (1K/s) than in MIES and UPS (1K/min). For this reason, the maximum desorption rate in MIES/UPS occurs about 15K earlier than in TPD.

The Au sample is cooled with liquid nitrogen to 100 K and exposed to water or methanol by backfilling the chamber. Exposures are stated in Langmuirs (L) ($1 \text{ L}=10^{-6} \text{ Torr} \cdot \text{s}$). It is expected that amorphous solid water and methanol are formed during the slow deposition of the respective vapours at temperatures below 120 K (see also ref. [11]).

3 RESULTS AND DISCUSSION

NaI and Cs halide layers were produced on ASW (MeOH) films at about 105K and annealed up to about 200K, and the electron emission from the ionization of the highest - lying states of H₂O, CH₃OH, and of iodide was studied [11,12]. **Fig. 1** presents (in arbitrary units) the variation of the probability for ionization of the states 5p_{3/2}I and 1b₁ H₂O (M_{3,4} MeOH; notation as in [12]) for NaI interacting with amorphous solid water (MeOH) films as a function of the film temperatures. For NaI/ASW, a gradual decrease of I(5p) becomes noticeable above 125K. An intensity minimum occurs at 134 K, close to the accepted water glass transition (T_g = 136 K) [7]. In the same region, water desorption becomes noticeable as manifested by the decrease of 1b₁ H₂O. As for CsI / ASW, I(5p) remains visible throughout the entire annealing procedure, although the intensity passes through a minimum. This is at variance with NaI / MeOH: here, I(5p) does disappear almost completely when annealing beyond 117 K (T_g = 120K [18]), -i.e. full solvation takes place. The same behaviour has been noticed for CsI / ASW and MeOH [11]. In ref. [11] this was attributed to the segregation of iodide at the ASW, but not at the solid MeOH surface. Surface segregation of heavy halide ions in liquid water, but not in liquid MeOH, has been predicted by classical MD calculations [2, 19] performed for NaI aqueous and MeOH solutions, and is subject of two recent reviews [9, 10]. Besides an increase of I(5p), we notice a decrease of the 5p_{3/2}I binding energy by about 0.6 (0.4)eV for ASW (MeOH), respectively. This decrease occurs around 135K, i.e. when, according to MIES, most of the water has already desorbed.

The portion of the total surface area occupied by iodide species (surface area accessed (ASA) by iodide [11]) can be accessed by both theory and experiment [11,12]. We can then estimate that the ASA of iodide is roughly 20 percent for both CsI and NaI. Theory predicts a value of ASA of 16 % for 1.2 M aqueous CsI solution [11]. For NaI we get a similar value, albeit smaller by ~2 %. The experiment and calculation are thus in a semi-quantitative agreement (note that the value of the experimental salt concentration is hard to obtain very accurately). For illustration, **Fig. 2** show, for illustration, the surface of a 1.2 M aqueous NaI solution, as obtained from a MD simulation [2]. Iodide anions are clearly seen at the surface, while sodium cations are absent (being, however, present in the subsurface).

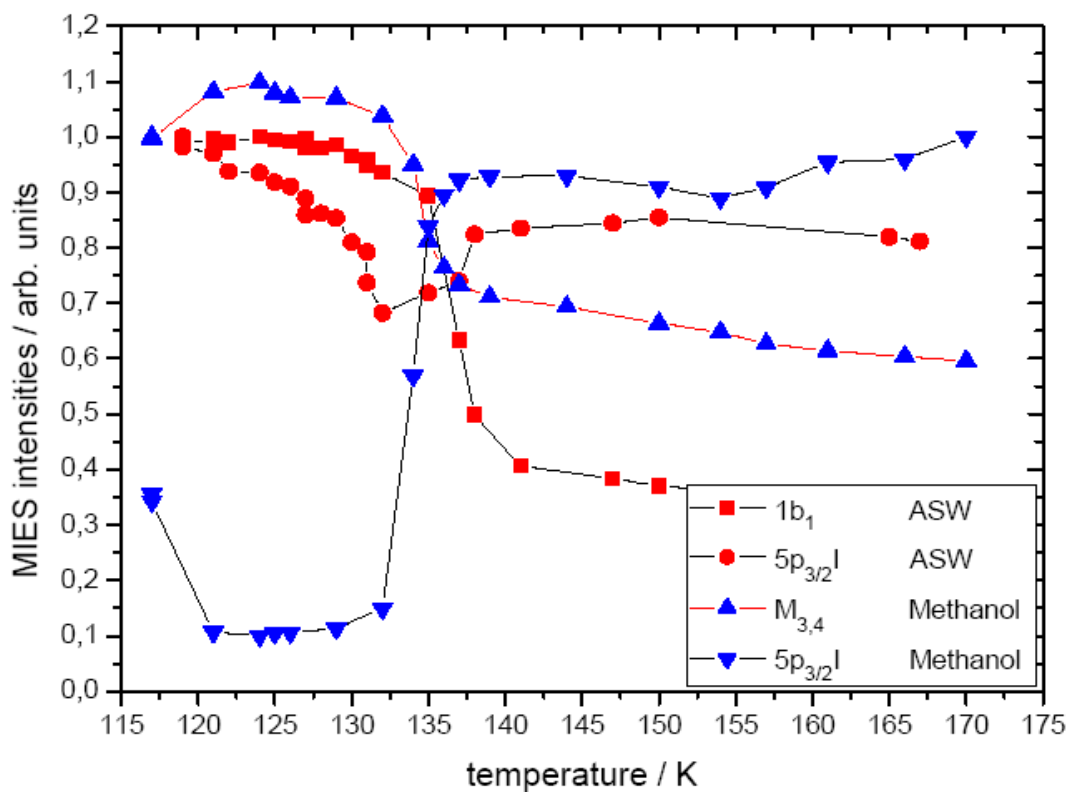


Figure 1 *Probabilities for the emission of electrons from the 5p_{3/2}I and 1b₁ H₂O states from iodide and water species, located in the top layer of the film produced by depositing 0.5ML NaI on amorphous solid water ASW and methanol (MeOH) films at 105K. Shown is the variation of the probabilities with the film temperature between 115 and 165K.*

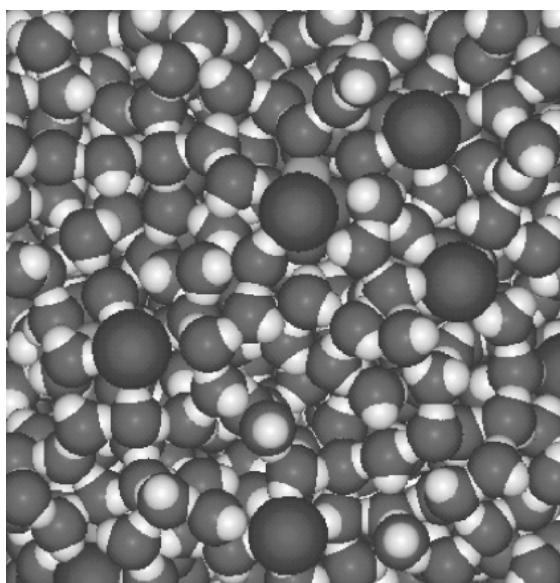


Figure 2 *A snapshot from a MD simulation of 1.2 M aqueous solution of NaI showing the structure of the surface. Large dark grey balls: iodide, small light grey balls: water oxygen, and white balls: water hydrogen.*

Summarizing, the comparison of experiments and computations suggests that viscous liquids, namely supercooled NaI (CsI) solutions (water and methanol), are obtained when depositing the salt molecules on amorphous solid films of the solvent molecules, and annealing the films above the respective T_g 's. As to solvation, these supercooled solutions behave similar as the corresponding liquid solutions. The formation of the supercooled solution precedes water desorption. These findings suggest that the local environment of the solute species, iodide and alkali, is similar to that seen by the same species in the respective normal liquids. The obvious consequence of this conclusion is that the water (MeOH) - ion interaction energies (binding energies), $I^- - H_2O$ (MeOH) in particular, and the electronic properties, ionization energies and the optical band gap, should follow from cluster - type calculations that simulate the local environment of the salt ions. For NaI / water such computations are available for room temperature solutions [20]. In the following, it will be demonstrated that this argumentation is indeed reasonable; in the following a comparison will be made between the MIES / UPS and TPD results [12] and the DFT results available for $NaI(H_2O)_n$ complexes [20].

TPD spectra recorded on mass 18 (H_2O) for neat water (20L) on Au (a), as well as for 0.7ML NaI deposited on ASW films of various thicknesses, and analogous data for the interaction of NaI with MeOH can be found in ref. [12]. The desorption of the neat "solvent", ASW, produces a narrow structure around 158K which we attribute to multilayer desorption. These peaks develop tails towards higher temperatures as the consequence of the NaI deposition. This was interpreted as follows: the NaI - solvent interaction gives rise to a broad range of H_2O binding energies, extending from about 42 kJ mol^{-1} (close to the values for desorption from the neat multilayer) to more than 60 kJ mol^{-1} for the strongest - bound species. It was shown that the remarkable broadening of the TPD spectra for NaI/ASW (as compared to neat water) towards higher temperatures under the influence of the supplied NaI molecules can be understood when adopting the following scenario: the preparation produces hydrated NaI structures, partially or fully dissociated in the sense of ref. [20]. When annealing, the increase of T first removes the weakest - bound

water molecules, -i.e. those not involved into the hydration of NaI species. This is followed by the removal of H₂O molecules from the largest hydrated structures present in the solution; further increase of the temperature leads to the removal of water molecules from increasingly smaller structures. This process can be visualized as the transition from NaI(H₂O)_n to NaI(H₂O)_(n-1) whereby n decreases with increasing temperature; decreasing values of n lead to increasingly stronger bound hydrated structures. A comparatively steep increase can be noticed for n = 3 → 2; it stems from the fact that below n = 4 all water molecules are in direct contact with the Na - I complex [20].

We proceed now to a discussion of the electronic properties of the NaI/ASW films as they emerge from the MIES / UPS spectra [12]; we adopt the same scenario as discussed above: we assume that the electronic properties of solvated iodide are determined by those of NaI(H₂O)_n complexes of the type studied in [20]. As all energies in fig.1 refer to the Fermi level, the vertical IPs with respect to the vacuum are obtained by adding WF (4.8eV for the top spectrum in fig.1(a)), as derived from the high - binding energy cut - off of the spectrum. For neat water (MeOH) this yielded 10.2 (8.9) eV for the distance between the valence band maximum and the vacuum level. In the same way we can determine ionization energy of 5pI. In order to discuss the observed solvation shift of I(5p) in ASW, -i.e. the decrease of the 5pI IP's during the anneal process from 8.9 eV by about 0.5eV, we rely on the electronic properties of NaI(H₂O)_n (n=1 to 6) clusters as computed by ref. [20]. The computed vertical IPs increase from 7.88eV for unsolvated NaI to values between 8.3 and 8.61eV for various n = 6 conformers; the increase is essentially up to n = 3. Thus, we are led to the conclusion that the solvation shift of the experimental IPs takes place when the coordination in the first solvation shell changes (for n < 4 while for larger n the IP will change comparatively little), -i.e. the observed shift of IP reflects the degree of solvation onto the electronic properties of the NaI - H₂O complexes. Thus, the essential aspects of the electronic properties can also be explained under the assumption of a supercooled solution whose local structure resembles that of the corresponding room temperature solution.

4 SUMMARY

We have studied the interaction of NaI and CsI with amorphous solid water (ASW) and methanol films, deposited on Au substrates. The deposition of the halides on the amorphous solid films (105K), followed by heating above the glass transition point, leads to the formation of supercooled halide solutions. For water, but not for methanol, we find a surface propensity of the iodide species of the solution. The same behaviour is predicted for the corresponding liquids by classical MD calculations. For NaI / ASW we have analyzed the ionization energy of I(5p_{3/2}) as well as the solvent desorption energies as a function of temperature on the basis of cluster DFT calculations, available for NaI - H₂O complexes. Our results suggest that the similarities observed for the iodide interaction with ASW (MeOH) and the corresponding liquids are based on the presence of similar NaI - solvent complexes in both cases.

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